E/CONF.39/A/130
17 Oct.1962
ORIGINAL : ENGLISH

UNITED NATIONS CONFERENCE
ON THE APPLICATION OF SCIENCE AND TECHNOLOGY
FOR THE BENEFIT OF THE LESS DEVELOPED AREAS

Agenda Item: A.5.3.1

South Africa

OBSERVATIONS ON THE TREATMENT OF SOME REFRACTORY ORES FROM SOUTH AFRICA

By P.A. LAXEN,
Head of the Chemical Processing Division,
Government Metallurgical Laboratory,
Johannesburg

and I.F. NAGY,
Research Officer,
Chemical Processing Division,
Government Metallurgical Laboratory,
Johannesburg

Papers have been contributed to the United Nations Conference on the Application of Science and Technology for the Benefit of the Less Developed Areas as working papers for that Conference. They are published as presented by the contributors, and the contents and the views expressed are those of the contributors. (See notes overleaf.)

NOTES

1. Papers selected for inclusion in General Sessions will be available at the Conference in the following official languages of the United Nations: English, French, Russian and Spanish.

2. Papers selected for inclusion in Specialized Sessions will be available at the Conference in only one of the above official languages.

3. Summaries of all papers, as submitted by contributors, will be available at the Conference in the following official languages of the United Nations: English, French, Russian and Spanish.

4. Papers and summaries will not be available for general distribution in advance of the Conference. They will be published in advance in limited quantities only for the use of delegations of participating governments and of other authorized participants. Post-Conference publication and general distribution of the Conference Proceedings will follow United Nations practices as laid down by the United Nations Publications Board.

OBSERVATIONS ON THE TREATMENT OF SOME REFRACTORY ORES FROM SOUTH AFRICA.

by:

P.A. Laxen,
Head of the Chemical Processing Division,
Government Metallurgical Laboratory,
Johannesburg.

and

I.F.Nagy,
Research Officer,
Chemical Processing Division,
Government Metallurgical Laboratory,
Johannesburg.

1. INTRODUCTION.

(a) In this paper 'refractory' ore is used to describe ores which in comparison with 'non-refractory' ores of the same type yield lower extractions of the desired constituents when treated under the conditions normal for the 'non-refractory' ores. To obtain acceptable extractions the refractory ore must usually be subjected to intensive treatment. Such treatment would be the use of a higher than normal concentration of reagents and/or high temperatures during leaching. Refractoriness in an ore is frequently attributable to the presence of 'refractory' minerals in the ore. In this paper examples are given of a uranium ore and a gold ore from South Africa in which the refractory behaviour is attributable to the nature or condition of the leaching solution rather than to minerals which are not easy to dissolve. A standard leach procedure is given which can be used to determine these instances. It is considered that the same technique could be used in obtaining fundamental data relative to a leach process.

(b) 'Refractory' Uranium Ores:

(i) The production of uranium in the Republic of South Africa is derived from the leaching by acid of the gold-uranium bearing conglomerate reefs of the Witwatersrand and Dominion Reef systems. Mineralogical examination has shown[1] the principal uranium mineral in these ores is uraninite. This mineral is readily soluble in solutions containing sulphuric acid and ferric sulphate. The commercial leaching procedure developed[2] for the extraction of uranium from South African ores required the use of sulphuric acid and manganese dioxide. The latter served to oxidise ferrous iron in solution to the ferric state, which then dissolved the uraninite.

$$UO_2 + 2Fe^{+++} \longrightarrow UO_2^{++} + 2Fe^{++}$$

(ii) In leaching on a plant scale the sulphuric acid and manganese dioxide are added at or near the commencement of the leach to the pulp containing approximately 60% solids. The acid pulp is agitated by air in a pachuca tank. The quantities of reagents have been determined by testwork on each ore, and depend on the reducing and acid consuming constituents of the ore. Sufficient sulphuric acid is added at the commencement of a leach so that the final solution contains 3 - 6 grams H_2SO_4/Litre. This yields a pregnant solution suitable

for feed to the ion-exchange columns for recovery of the uranium in solution.

(iii) Ore samples from each prospective uranium mine were tested at the Government Metallurgical Laboratory in Johannesburg to ascertain the optimum conditions for leaching and the uranium extractions possible. If the uranium in all the ores were present as uraninite uniformly high extractions could be anticipated, since all the ores were, in major aspects of composition, similar. Many ores gave the expected high uranium extractions when leached at ambient temperatures for about 12 - 16 hours with reasonably low additions of sulphuric acid and manganese dioxide. Ores from certain areas, however, gave unexpectedly low uranium extractions. Ores from the Dominion Reef, for example, gave uranium extractions of 65 - 75% compared with the approximately 90% extractions from ores from the Kimberley Reef under similar conditions. High leach temperatures and higher reagent additions improved the uranium extractions from the former. The uranium not dissolving under normal leach conditions was thought to be attributable to the presence of an unidentified, highly refractory uraniferous mineral.

(iv) In a programme to investigate these 'refractory' ores it was found that the 'normal' leach procedure, of adding the sulphuric acid and manganese dioxide at the beginning of the leach, was inadequate for conducting comparative leach tests on different ore samples as will be explained later. A standard leach procedure was developed which gave constant leach conditions throughout the leach period irrespective of the ore sample being treated. The results obtained by the use of this simple, standard leach procedure - called the 'dilute leach' - changed previously held opinions as to the refractoriness of these ores, and also resulted in a clearer understanding of the factors in the leaching of these and other ores(3).

(v) It is felt that this standard leach technique, which is purely a laboratory technique, may have application in other leaching investigations and is accordingly described in this paper. The results obtained on an ore from the Dominion Reef illustrate the application of the 'dilute leach' procedure.

(c) Refractory Gold Ores:

(i) Many of the gold ores from the Barberton district of the Transvaal are 'refractory'. Frequently these refractory ores contain sulphides which occlude the gold values. These ores requre treatment such as roasting or pressure leaching to oxidise the sulphides and render the gold in them available to dissolution by cyanidation. Ores from the oxidised zone in this area, however, have usually responded directly to cyanidation. One ore sample from the Princeton mine, submitted for gold extraction tests, had oxidised from atmospheric oxidation over twenty years in a surface dump. Due to its oxidised nature good response to cyanidation was expected from this ore. Normal cyanidation tests, however, yielded poor gold extractions. The standard leach procedure - the 'dilute leach' referred to above - was applied to the cyanidation testing of this ore. The improved results obtained by this procedure showed that the refractory behaviour was attributable to an effect of the ore on the leach solution and not to the presence of a refractory mineral in the ore.

2. STANDARD LEACH PROCEDURE (DILUTE LEACH).

(a) In a normal leach procedure, with the reagents added at the commencement of the leach period, the concentrations of the reagents will decrease throughout the leach as they are consumed. In the acid leaching of uranium ores the sulphuric acid concentration in the leach will decrease from a high initial figure - some 30 to 60 grams H_2SO_4/litre - to the 3 - 6 grams H_2SO_4/litre at the end of the leach. Likewise the concentration of Fe^{+++} will decrease as it oxidises various constituents in the ore. As mentioned earlier this normal leach procedure was found inadequate

when investigating and comparing the leach characteristics - i.e. behaviour during leaching - of different ore samples. Any variations in the proportion of acid consuming constituents or reducing constituents between different samples meant that the initial additions of sulphuric acid and manganese dioxide had to be varied from sample to sample so that the final leach solutions could be as similar as possible with respect to concentrations of H_2SO_4, Fe^{+++} and Fe^{++}. During the leach tests, however, the all important concentrations of H_2SO_4 and Fe^{+++} would differ from the testing of one ore to another, possibly being similar only at the end of the leach. In addition, the effect, if any, attributable to a constituent which dissolved from an ore during leaching could vary quite considerably from one ore sample to another as the proportion of the particular constituent in different samples varied, e.g. phosphate derived from the dissolution of acid soluble phosphate minerals.

(b) In order to be able to compare different samples under identical leach conditions a standard leach procedure was required. The procedure adopted has been called the 'dilute leach'. In this standard leach the ratio of solution to ore was increased from the 0.67/1, approximately, in the normal leach to 10/1. Ten grams of ore was usually used in 1000 mls of leach solution. The dilute slurry was agitated by rolling in a bottle in a water-bath maintained at constant temperature.

(c) In uranium leaching the leach solution was made up to definite concentrations of sulphuric acid and ferric sulphate. The large excess of leach solution relative to a small weight of sample resulted in virtually no change in the reagent concentrations during the leach period. The acid consuming constituents and reducing constituents in 10 grams of ore were too small to affect the concentrations of leach reagents. The leach residues were analysed by a method involving the extraction of uranium into tributyl phosphate followed by colorimetric estimation.

(d) This leach procedure, it was found, could be applied to any uranium ore sample, and any combination of reagents could be tested on any ore at any leach temperature. An application of this leach procedure which became obvious was that the effect on the leach of any ion could be determined by merely varying the addition of that ion in the dilute leach, e.g. the effect of phosphate ion was determined by varying the concentration of phosphate in the leach solution from nil up to, say 0.5 grams P_2O_5/litre in successive tests.

(e) Using this 'dilute leach' procedure ore samples from the different uranium-bearing reefs of South Africa were tested under a wide variety of conditions and the information obtained proved very valuable in understanding the behaviour of the different ores under plant scale leaching. Some of the results obtained on 'refractory' ore from the Dominion Reef are given later.

(f) In applying the principle of the 'dilute leach' to a refractory gold ore from the Barberton area in the Eastern Transvaal dilution ratio of 4Q/1 of solution to solid were used, i.e. 100 grams of ore in 4 litres of leach solution. Agitation was effected by rolling in an open glass bottle, except in particular tests when air agitation was used. The effect of cyanide and lime concentrations and of various impurities could be determined under standardized conditions. In these tests the residues were analysed for gold by the normal fire-assay method.

3. RESULTS AND DISCUSSION:

(a) Refractory Uranium Ore from the Dominion Reef.

(i) Uranium Extractions from 'Normal' Leach tests.

a. Table 1 illustrates the results obtained on this ore under various 'normal' leach conditions.

b. The conditions used in test No. 1 were adequate for the complete dissolution

of uraninite but an extraction of only 73.8% was in fact obtained. Even with the more severe conditions of the remaining tests complete extraction of the uranium was not achieved.

(ii) Comparison of 'Dilute' and 'Normal' Leach Tests.

a. Table 2 contains typical results of the 'dilute' and 'normal' leach tests.

b. The normal leach tests used for comparison were tests in which the final acid concentration in the leach solutions were similar to the constant acid concentration used in the 'dilute leach' tests. In other words the acid concentrations in the comparative 'normal' leach tests had actually been higher than those in the 'dilute leach' tests. The initial acid concentration corresponding to the reagent addition for each 'normal' leach test is given in Table 2.

c. As shown the extractions in the 'dilute leach' tests were unusually high. By means of the 'dilute leach' practically complete dissolution of the uranium - up to 98.5% - in this ore was obtained at 50°C with moderate acid concentrations. Even at 28°C extractions of 90% were possible with 20 grams H_2SO_4/litre. These results were not compatible with the earlier thoughts of a refractory ore.

(iii) Factors in the Acid Leaching of the Dominion Reef 'Refractory' Ore.

a. By merely altering the dilution ratio during leaching - i.e. by minimizing the effect of the ore sample on the leach solution - this ore had been converted from a 'refractory' ore to an 'amenable' ore. A series of 'dilute leach' tests was conducted in which many possible factors were tested and it was found that two factors were important in explaining the 'refractory' behaviour of this ore during plant-scale leaching. These two factors were :-

i. Concentration of Phosphate ions in the Leach Solutions.
ii. Oxidation Potential of the Leach Solution.

i. Effect of Phosphate Concentration.

Table 3 shows the results obtained on addition of low concentrations of phosphate. This deleterious effect of phosphate is not attributable to any complexing of ferric ions since 0.5 grams Fe^{+++} was all that was required for maximum dissolution, and hence the 4 grams Fe^{+++}/litre present represented a large excess of Fe^{+++}. The addition of phosphate at the end of the leach period had no deleterious effect on extraction, showing that this effect of phosphate was not attributable to any precipitation effect. The phosphate concentration in a leach solution from the Dominion Reef ore was usually about 0.25 grams P_2O_5/litre. Ores that gave good uranium extractions under normal conditions at ambient temperatures were unaffected by the presence of phosphate.

ii. Effect of the Oxidation Potential.

The oxidation potential of the leach solution, which is controlled and indicated by the Fe^{+++}/Fe^{++} ratio, was investigated by the 'dilute leach' technique and it was found that uranium dissolutions from many South African ores were practically unaffected by variation in the Fe^{+++}/Fe^{++} ratio. The 'refractory' ore from the Dominion Reef was, however, affected. This is illustrated by the results in Table 4. These results were obtained by dilute leach tests.

(b) Refractory Gold Ore from the Princeton Mine of the Barberton Area.

(i) Comparison of Normal and Dilute Leach Tests.

a. The initial cyanidation tests on this sample gave low gold extractions. In a 'dilute leach' test - i.e. with a high liquid/solid ratio of 40/1 - a marked improvement in gold extraction was obtained. as shown in Table 5.

b. The improvement in gold extraction in the 'dilute leach' test indicated that the refractory behaviour of this ore was in large measure due to the leach solution. Using the 'dilute leach' procedure the effect of various factors on gold extraction from this ore was ascertained.

(ii) Effect of Cyanide Concentration.

a. With constant CaO additions and a dilution of 40:1 liquid:solid the cyanide concentration was varied in a series of tests. The results obtained are given in Table 6.

b. Increasing the cyanide strength of the leach solution beyond 0.1% was apparently dissolving some constituent of the ore which was then adversely affecting gold dissolution. These tests showed that 86.5% of the gold in this ore was soluble in cyanide solutions of normal concentrations and not associated with a refractory mineral.

(iii) Effect of CaO Concentrations.

a. The results of 'dilute leach' tests in which the effect of increasing CaO additions was determined are shown in Table 7.

b. With 0.1% KCN there was only a slight effect due to varying the CaO concentration, with a concentration of .011% CaO in test 2 giving the maximum dissolution. The deleterious effect of high cyanide concentrations shown in Table 6 and in test 7 of Table 7 can apparently be offset by not adding CaO, as in test 6 of Table 7.

(iv) Effect of Air Agitation.

a. At dilutions of 40:1 there was no beneficial effect due to agitation by air as compared with agitation by bottle rolling. At dilutions of 1:1 there was a slight improvement of gold extraction with air agitation.

4. CONCLUSIONS.

(a) A standard, laboratory leach test, termed the 'dilute leach', proved useful in understanding the 'refractory' behaviour in plant-scale leaching of certain uranium ores. The near complete extractions obtained by the 'dilute leach' procedure, under what might be termed reasonable reagent concentrations, eliminated the possibility of a highly refractory uraniferous mineral being present in ores from the Dominion Reef. The 'refractory' behaviour of this ore in plant-scale leaching was attributable to effects of the ore on the leach solution and to the presence of a mineral in the ore that was not unusually difficult to dissolve but rather was sensitive to, or affected by, the changes in the leach solutions brought about by the ore. The important effects of the ore on the leach solutions were the introduction of phosphate ions - dissolved from constituents of the ore - and the lowering of the oxidation potential of the leach solution. Ores which gave good extractions in normal plant-scale leaching were unaffected by these factors under the conditions used for testing.

(b) The principle of eliminating the effect of the ore on the leach solution by using the 'dilute leach' technique again proved effective in the testing of a 'refractory' gold ore. This ore gave good gold extractions on cyanidation

with the 'dilute leach' establishing that the 'refractory' behaviour in 'normal' cyanidation tests was not due to a refractory gold-bearing mineral, but to an effect of the ore on the leach solution.

(c) The 'dilute leach' technique appears to have application in the testing of refractory ores. The technique can be applied to the determining of the important factors in a leach system.

REFERENCES.

1. Liebenberg, W.R. The Occurrence and Origin of Gold and Radioactive Minerals in the Witwatersrand System, the Dominion Reef, the Ventersdorp Contact Reef and the Black Reef. Trans. Geol. Soc. S.Afr. LVIII p.101 (1955).

2. Gaudin, A.N., Schuhmann, R. and Dasher, J. South Africa: Extraction Process for Gold-Uranium Ores. J.Metals 8 p.1065 (1956).

3. Laxen, P.A. Observations on the Dissolution of Uranium from Ores of the Witwatersrand Progress Report (Leaching) No.259 and 261. Government Metallurgical Laboratory, Johannesburg.

TABLE 1.

Uranium Extractions from the Dominion Reef. (Leach Time - 18 Hours.)

Test No.	Reagents H_2SO_4 lb/t	Reagents MnO_2 lb/t	Leach Temp. °C	Final H_2SO_4 g.p.l.	Leach Solutions Fe^{+++} g.p.l.	Leach Solutions Fe^{++} g.p.l.	% U_3O_8 Extraction.
1	50	10	28	7.8	4.5	0.3	73.8
2	80	20	"	20.8	5.0	0.07	79.3
3	150	10	"	70.7	6.2	0.07	88.8
4	300	10	"	168.9	7.3	0.07	94.5
5	60	18	50	9.5	4.4	1.4	82.3
6	80	5	"	20.0	4.1	2.8	87.1
7	150	10	"	58.0	6.4	2.03	93.9
8	300	10	"	150.0	7.7	2.14	97.0

TABLE 2.

Comparison of 'Dilute leach' Tests and 'Normal' leach Tests. (Leach Time - 18 hours.

	Normal Leach (Soln/Ore = 0.67/1)							'Dilute leach' (100/1 soln/ore)		
Test No	Reagents H_2SO_4 lb/t	Reagents MnO_2 lb/t	Initial Conc. H_2SO_4 g.p.l.	Final Leach Soln. H_2SO_4 g.p.l.	Fe^{+++} g.p.l.	Fe^{++} g.p.l.	% Uranium Dissol.	Leach Solution H_2SO_4 g.p.l.	Leach Solution Fe^{+++} g.p.l.	% Uranium Dissol.
28°C										
1	50	10	37.5	7.8	4.5	0.3	73.8	8.0	4.0	83.8
2	80	20	60.0	20.8	5.0	0.07	79.3	20.0	4.0	90.1
50°C										
1	60	18	45.0	9.5	4.4	1.4	82.3	8.0	4.0	96.4
2	80	5	60.0	20.0	4.1	2.8	87.1	20.0	4.0	98.5

TABLE 3.

Effect of Phosphate on Dominion Reef 'Dilute Leach' Tests.

Phosphate Added g.p.l. P_2O_5	nil	0.25	0.5	Leach Conditions
% Uranium Extraction	78.2	71.0	69.5	4 g.p.l. H_2SO_4 4 g.p.l. Fe^{+++} 28°C 18 hours.

TABLE 4.

Effect of Fe^{+++}/Fe^{++} Ratio on Dominion Reef in 'Dilute Leach' Tests.

Fe^{+++} conc. g.p.l.	4	3	2	1	Leach Conditions.
Fe^{++} " g.p.l.	nil	1	2	3	4 g.p.l. H_2SO_4
Fe^{+++}/Fe^{++} ratio	4/0	3/1	2/2	1/3	28°C
% Uranium extraction	78.2	70.2	69.9	67.6	18 hours.

TABLE 5.

Improvement in Gold Extraction at High Dilution.

Normal Dilution Soln/Ore = 1/1			High Dilution-Dilute Leach Soln/Ore = 40/1			
Initial Cyanide Conc %KCN	Initial Lime Conc %CaO	% Gold Extrn	Initial Cyanide Conc. %KCN	Initial Lime Conc. %CaO	% Gold Extn.	Leach Conditions 24 hours 25°C
0.5	0.168	35.1	0.5	.0095	73.0	

TABLE 6.

Effect of Cyanide Concentration in 'Dilute Leach' Tests.

Test No	Cyanide Conc. %KCN	% Gold Extraction	Leach Conditions.
1	0.05	85.3	Soln/Ore = 40/1
2	0.10	86.5	24 hours
3	0.25	75.8	25°C
4	0.50	73.0	Initial CaO conc. = .011% CaO
5	1.00	66.3	

TABLE 7.

Effect of CaO Addition in 'Dilute Leach' Tests.

Test No.	Cyanide Conc. %KCN	Lime Conc. in Soln. %CaO	% Gold Extraction	pH of Final Soln.	Leach Conditions.
1	0.1	nil	83.7	10.1	Soln./Ore = 40/1
2	"	.011	86.5	11.0	24 hours
3	"	.025	83.0	11.6	25°C
4	"	.063	81.7	12.1	
5	"	.168	81.0	12.4	
6	1.0	nil	81.1		
7	"	.011	66.3		

1085 E - Oct.1962 - 1,600